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Atomic layer deposition of TiO_2 from tetrakis-dimethylamido-titanium and ozone

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Abstract−Ozone (O_3) was employed as an oxygen source for the atomic layer deposition (ALD) of titanium dioxide (TiO_2) based on tetrakis-dimethyl-amido titanium (TDMAT). The effects of deposition temperature and O_3 feeding time on the film growth kinetics and physical/chemical properties of the TiO_2 films were investigated. Film growth was possible at as low as 75 °C, and the growth rate (thickness/cycles) of TiO_2 was minimally affected by varying the temperatures at 150-225 °C. Moreover, saturated growth behavior on the O_3 feeding time was observed at longer than 0.5 s. Higher temperatures tend to provide films with lower levels of carbon impurities. The film thickness increased linearly as the number of cycles increased. With thicker films and at higher deposition temperatures, surface roughening tended to increase. The as-deposited films were amorphous regardless of the substrate temperatures and there was no change of crystal phase even after annealing at temperatures of 400-600 °C. The films deposited in 0.5 mm holes with an aspect ratio of 3 : 1 showed an excellent conformality.

Key words: TiO_2, Ozone, Atomic Layer Deposition (ALD), TDMAT, Crystalline

INTRODUCTION

Titanium dioxide (TiO_2) is a very useful material for various industrial applications, due to its attractive physicochemical properties [1-5]. The growth of TiO_2 films has been studied using a number of various dry or wet processes [6-10]. Among these techniques, atomic layer deposition (ALD) has recently received great attention for the preparation of TiO_2 thin films [11,12] due to high conformality on high-aspect ratio features and excellent uniformity of the deposited films over large areas. ALD is a modified form of CVD (chemical vapor deposition), with one of the main differences between CVD and ALD being the method of introducing reactants into the chemical reactor, CVD uses simultaneous introduction of reactants and can utilize both gas and surface reactions, while ALD uses discrete introduction of reactant pulses with an intermediate purging step, restricting the reaction to absorbed species on the substrate surface, leading to self-limited growth.

While the most commonly used precursor of TiO_2 ALD is titanium tetrachloride ($TiCl_4$), it is not ideal due to its corrosive nature. Thus, a search for alternative precursors of TiO_2 ALD is needed. Titanium tetraisopropoxide (TTIP) ($Ti[OCH(CH_3)_2]_4$) and tetrakis (dimethylamido) titanium(TDMAT) ($Ti[N(CH_3)_2]_4$) have been the most frequently explored as potential alternative precursors to $TiCl_4$ [13-19].

For the oxygen source, water (H_2O) has been commonly used for TiO_2 ALD, regardless of the Ti precursor used. However, H_2O tends to physisorb strongly on reactor surfaces and thus can lead to a longer purge time needed to remove the physisorbed H_2O sufficiently. Moreover, the necessity of the low deposition temperature for coatings on thermally sensitive materials, i.e., polymers or small organic materials, drives the need to find alternative oxygen sources because the purging for H_2O removal becomes difficult with lower deposition temperatures. Ozone (O_3) is a strong oxidizing agent and is highly volatile, which makes it one of the most promising alternative oxygen sources in TiO_2 ALD [16,17,20]. However, reports using O_3 for TiO_2ALD and especially TDMAT- O_3 system have not been reported yet. Therefore, this study was conducted to explore O_3 as a potential alternative to H_2O in TDMAT-based TiO_2 ALD process.

EXPERIMENTAL

The TiO_2 films were prepared on a p-type Si and soda lime glass in a shower-head equipped vertical-flow reactor that was designed to process 200 mm wafers. The reactor was a warm wall reactor with the wall temperature of about 100 °C. Tetrakis (dimethylamido) titanium (TDMAT) was purchased from UP Chemicals and used without any further purification steps. Because this precursor is very sensitive to water vapor in the air, its handling was performed exclusively in a dry box under Ar gas environment. The vaporized TDMAT was introduced to the reactor from a container, held at 30 °C by bubbling helium (150 sccm), and the vapor delivery lines were heated at 60 °C to prevent precursor condensation. Ozone was produced by an O_3 generator (MKS, AX8560). A mixture of oxygen (1,000 sccm, 99.999%) and catalytic nitrogen (5 sccm) was used to generate ~12 wt% O_3 and the O_3 concentration of about 250 g/nm^3. A gas line for delivering of O_3 was maintained at a temperature of about 115 °C because it was reported that 99% of O_3 remained intact from thermal decomposition at 115 °C, if there were no chemical reactions on the inner surfaces of the gas line [18,21]. One deposition cycle consisted of exposure to the precursor, an argon (Ar, 200 sccm) purge, plasma exposure, and another Ar (500 sccm) purge. The processing pressure was about 0.8 torr, and the substrate temperature was in the range of 75-225 °C. The pressure of the reactor was meas-

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ured by a diaphragm gauge and was controlled by automatic throttling the exhaust line to the pump.

Prior to the deposition of the films, the Si substrates were cleaned with the RCA method. The glass was cleaned ultrasonically first in acetone for 10 min, followed by rinsing with deionized water and then in isopropyl alcohol (IPA) for 10 min followed by rinsing with deionized water, after which they were rinsed with water and dried with N_2. The TDMAT pulse time was fixed to 0.5 s for all experiments, and the O_3 feeding time was varied from 0.5 to 1.5 s. Flow rates of Ar purging gas were 200 and 500 sccm for TDMAT and O_3, respectively. Also, the Ar purge time after the precursor pulse and O_3 injection was 15 s and 30 s, respectively.

The thicknesses of the samples were mainly determined using X-ray reflection (XRR) and also examined using a cross-sectional high resolution transmission electron microscopy (HRTEM) as an auxiliary way. More than three different points of the samples were examined to check the uniformity of the film thickness. The impurity levels in the films were analyzed by X-ray photoelectron spectroscopy (XPS) using Al Kα X-rays with resolution of 0.1 eV at 150 W of power. The surface roughness and step coverage of films were evaluated using atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively. The step coverage was examined with a TiO_2 film deposited on the 0.5 μm wide and 1.5 μm deep holes. Also, the crystallinity of the TiO_2 films was examined using TEM and X-ray diffraction (XRD), using a Cu Kα X-ray source.

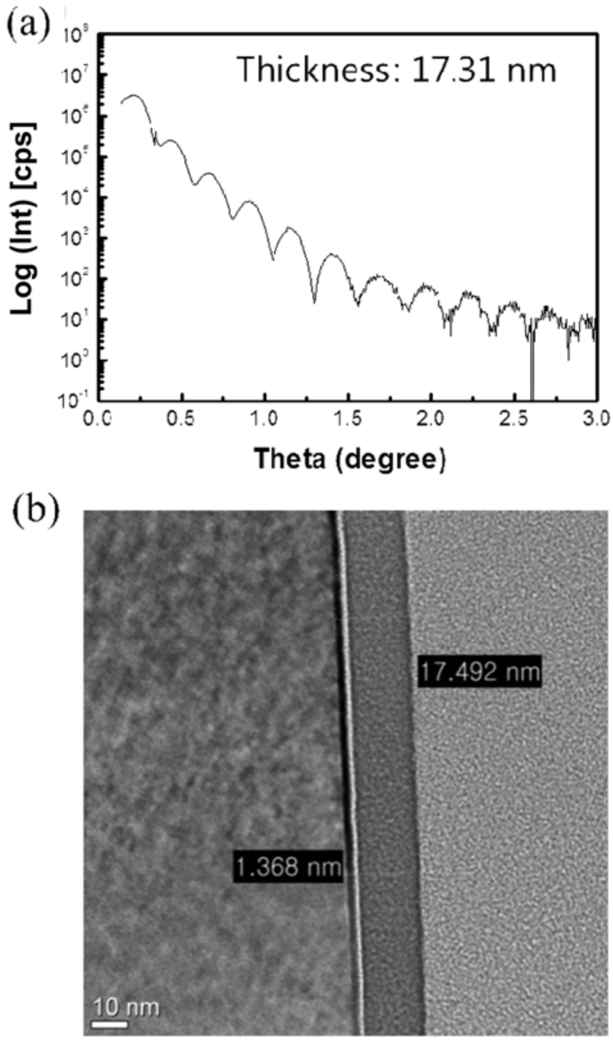

Fig. 1. Thickness of the TiO_2 films estimated by (a) XRR and (b) high resolution TEM.

RESULTS AND DISCUSSION

Film growth rate was obtained from the calculated values of the film thickness divided by the number of cycles. The TiO_2 film thickness was mainly measured using XRR, but a few samples were analyzed with a cross-sectional HRTEM to confirm the thickness measured by XRR. Fig. 1 shows a typical XRR spectrum, obtained from the samples deposited at 150 °C using 400 ALD cycles. The estimated TiO_2 thickness using XRR and the thickness measured by TEM was 17.31 nm and 17.49 nm, respectively, indicating that thickness measured by both techniques is very close. Also, there was only about ±2.5% difference in the film thickness estimated by XRR and TEM, even in relatively thinner or thicker films than 17.49 nm thick.

A 0.5 s TDMAT pulse was selected through this work to supply an abundant dose of the precursor, based on the separate experimental results on the film growth rate versus TDMAT pulse time. A relatively long purging time of 15 s for the TDMAT was used to ensure sufficient reactant purge for self-limiting film growth. No apparent growth rate change occurred with purging times longer than 10 s for the TDMAT, indicating that the purging time of 10 s after the precursor pulse is sufficient to remove reactants and byproducts from the reactor.

The effect of the ozone pulse time on the growth rate of the films was also evaluated at 150 °C by varying the time from 0.5 to 1.5 s with a fixed purging time of 15 and 30 s for the TDMAT and O_3, respectively. A 30 s purging time for the O_3 was used although a 10 s precursor pulse was enough to avoid cross contamination of the reactants in the reactor. No marked change in the growth rate (~0.044 nm/cy) was observed by varying the O_3 feeding time of longer than 0.5 s, indicating a self-limiting film growth. Here, it is interesting to note that the growth rate of O_3-based TiO_2 ALD is

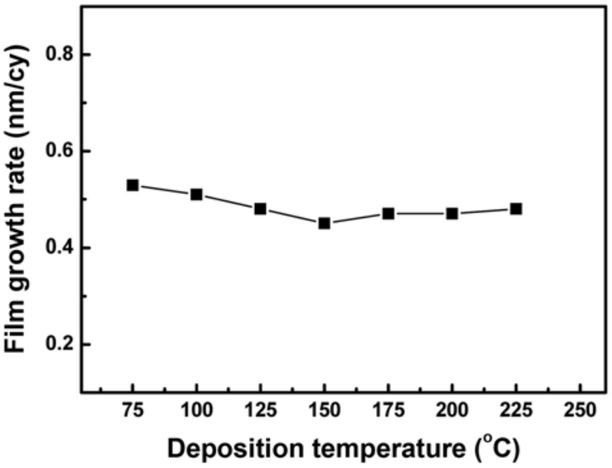

Fig. 2. The effect of deposition temperature on film growth rate.

higher than that of the water or hydrogen peroxide-based TiO_2 ALD by about 10-20% [18,19]. This suggests that the type of oxidants plays an important role for the formation of ALD TiO_2 films. The increase in the saturated ozone growth rate is attributed to the higher reactivity of ozone oxidant to water or hydrogen peroxide.

To determine the appropriate ALD process window, film growth rates were evaluated at temperatures of 75-225 °C (Fig. 2). The films were grown with 500 cycles at a fixed condition of 0.5 s of TDMAT pulse, 15 s of TDMAT purge, 1 s of ozone, and 30 s of O_3 purge. As the substrate temperature increased from 75 to 150 °C, the film deposition rate decreased slightly from 0.053 nm/cy to 0.044 nm/cy. A further increase in deposition temperatures resulted in an almost saturated growth rate of 0.047-0.048 nm/cy, regardless of the substrate temperatures of 175-225 °C. In an ideal case of ALD, the growth rate (thickness per cycle) remains constant with varying substrate temperatures within the process window. However, a small reduction in the growth rate with increasing deposition temperatures is commonly observed, due to a loss of reactive surface groups [15, 21-23] or the excess condensation of the precursor at lower temperature, i.e., physisorption of the precursors. In the case of excess precursor condensation, the thickness of the film would be restored to a saturated level with sufficiently longer reactant purge time. However, excess condensation is not likely in our system because volatile reactants such as TDMAT and O_3 were used.

To define the cause of lowering growth rates with the deposition temperature increase from 75 to 150 °C, compositional analysis was performed. Fig. 3 shows a typical XPS spectrum of the O_3-based film deposited at 150 °C, and compositional analysis of the tested samples are summarized in Table 1. As can be seen in Table 1, all film contains carbon and/or nitrogen impurities irrespective of the deposition temperature. In addition, excess oxygen within the films is observed clearly, and a similar phenomenon was reported previously in other ozone/alky amide systems for metal oxide film, such as TiO_2 and HfO_2 [17,21,24]. The TiO_2 films grown in this study demonstrated that the deposition temperature minimally impacted the O/Ti ratio. The impurities of carbon and nitrogen contents decreased as the deposition temperature increased. The films grown at 75 °C contained about 8.57% of carbon, which is the highest level in this study. Although the cause of the high carbon content in the films made at lower deposition temperature remains unclear, we speculate that the insufficient removal of by-products may partially contribute to the observed higher growth rate at lower temperatures.

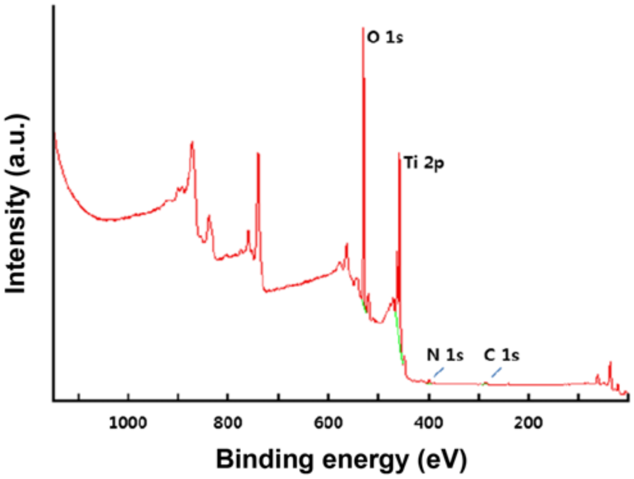

Fig. 3. XPS spectrum of the film deposited at 150 °C.

Table 1. Impurities of the TiO_2 films (from XPS analysis)

Deposition temperature (°C)	O/Ti ratio	N contents (at %)	C contents (at %)
75	2.21	4.86	8.57
150	2.21	2.06	4.35
225	2.20	N.D.*	1.74

N.D.*: No detection

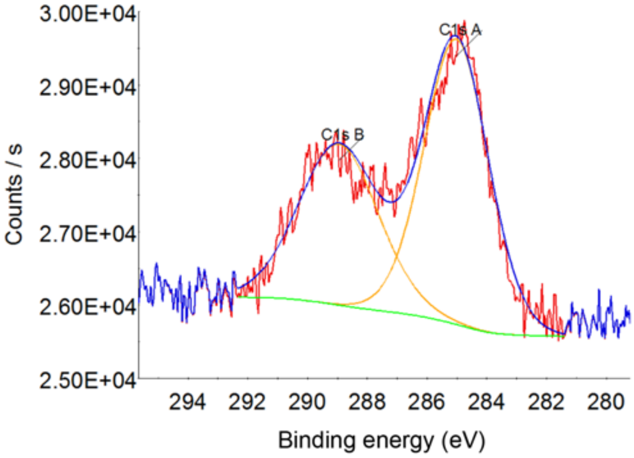

Fig. 4. XPS spectrum of typical TiO_2 films for C 1s.

Fig. 4 shows the XPS spectrum of typical TiO_2 films for C 1s, with peaks appearing at two different positions. The peak positions at 285.0, and 289.1 eV correspond to C-C bonding and C=O bonding, respectively. It is noteworthy that the peak intensity of the films formed at a low temperature at 289 eV is higher than that of the films made at a high temperature. More interestingly, no peak was observed at around 282.5 eV, which represents carbidic carbon [25]. This suggests that all carbons in the films exist as organic-bonded forms rather than the chemically formed Ti-C structure. The XPS spectrum (not shown) of Ti 2p and O1s revealed metallocene and carbonates peaks at 457. 2 and 532 eV, respectively, supporting that carbon impurities exist as organic forms. This provides evidence that the increased film growth rate with decreases in the deposition temperatures below 150 °C is due to incomplete desorption of the by-products, i.e., fragmented carbon compounds, in the deposits. In other words, a higher deposition temperature provides a higher activation energy for desorption of carbon containing species, which means that more carbon-containing species can be removed from the surface by O_3 at higher deposition temperatures. With regards to the nitrogen impurities, they existed as the form of nitride (Data is not shown).

Typical features of ALD processes are a linear relationship of the film thickness to the number of cycles and the excellent conformality. At 150 °C, the film thickness linearly increased with the number of cycles as shown in Fig. 5. The film growth rate (slope of the Fig. 5) was estimated to be about 0.044±0.015 nm/cycle. No detectable nucleation delay was observed on the Si substrate. The surface

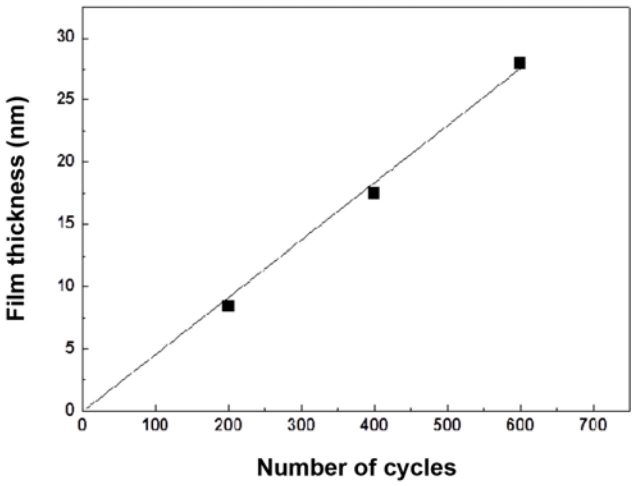

Fig. 5. Film thickness as a function of number of cycles.

roughness increased with increasing film thickness. At the same thickness, increased surface roughening was observed with increasing deposition temperatures. The root mean square (RMS) roughness of the films of 8.67 and 28 nm thick films was 0.221 and 0.298 nm, respectively. The value of RMS was about 3% of the 8.67 nm film thickness. However, where the film was 28 nm thick, the value of RMS was about 1% to the film thickness. This may suggest a relatively high nucleation rate of the TiO_2 on the TiO_2 surface compared to the growth rate of the TiO_2 on the Si substrate. Furthermore, the TiO_2 film deposited on a hole patterned substrate demonstrated an excellent step coverage, indicating the conditions investigated are of the ALD-type (Fig. 6).

Fig. 7 shows the XRD patterns of the samples deposited at 100, 150, and 200 °C, showing that the films deposited at all temperatures are amorphous. There was no observed correlation of crystallinity and the film thickness. Moreover, the amorphous structure of the as-deposited TiO_2 film (50 nm thick) was not changed even with post annealing at high temperatures of 400-600 °C in the air for 3 hrs, indicating that carbon impurities in the film can affect the crystallization kinetics.

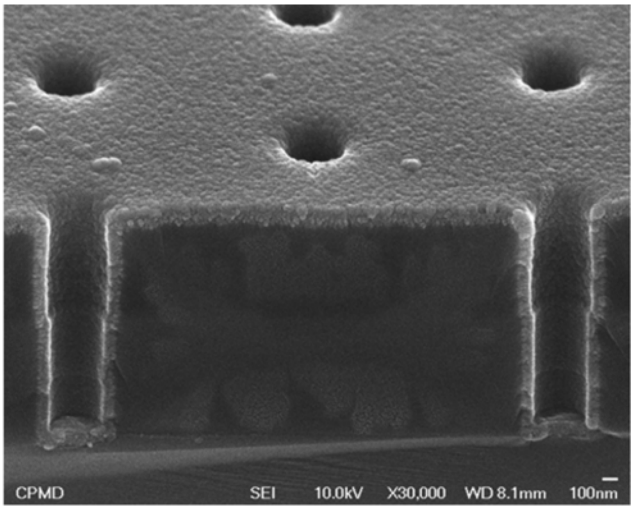

Fig. 6. A cross-sectional SEM of TiO_2 deposited on a hole pattern.

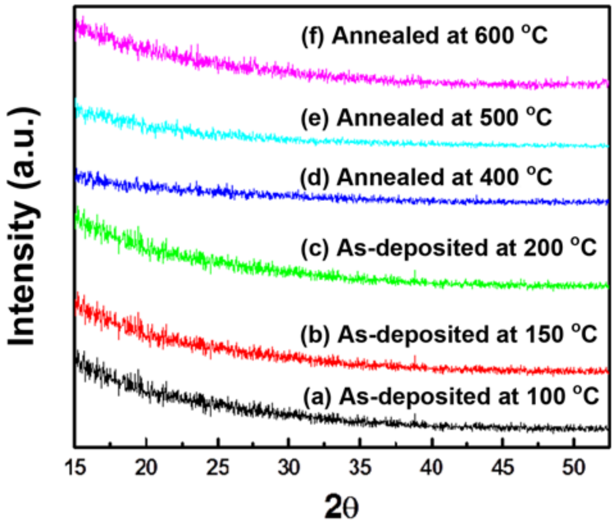

Fig. 7. XRD patterns of the TiO_2 films deposited at (a) 100 °C, (b) 150 °C, and (c) 200 °C; XRD patterns of the TiO_2 films deposited at 150 °C after annealing at (d) 400 °C, (e) 500 °C, and (f) 600 °C in air.

CONCLUSIONS

We demonstrated that TiO_2 can be prepared at low temperatures without incubation on Si substrates by using O_3 as an oxygen source. Self-limiting reaction is possible, as supported by a saturated film growth rate and the linear property of the film growth depending on the number of cycles, along with excellent conformality. Films deposited at 75-220 °C contained carbon impurities that may contribute to the hindering of crystallization of not only the as-deposited films but also the annealed films at high temperatures. The removal of the carbon impurities is essential for crystallization of the TiO_2 film prepared by TDMAT and O_3.

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